

SCANNING ELECTRON MICROSCOPE STUDY  
ON THE CATALYTIC GASIFICATION OF COAL

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INTRODUCTION

In previous papers (1,2), it has been reported that coals pretreated with liquid ammonia can be gasified more easily than untreated coals, especially when they are impregnated with nickel catalysts. The effectiveness of nickel catalyst varies with such parameters as the method of nickel loading, the kind of nickel salt, the condition of reduction of salt to metallic state, and others. According to circumstances, nickel does not necessarily act as effective catalyst. In order to obtain a higher catalytic activity, it is essential to understand how a nickel particle catalyzes the gasification reaction. Some particles may be active, and others may be less active. We then have to find the way of nickel loading to produce only such active particles. Thus, we can maximize the catalytic activity of nickel for coal gasification. The microscopic observation is known to be one of the most useful tool for understanding the behavior of metal catalyst on carbon gasification (3,4,5). Scanning electron microscope (SEM) studies on catalytic coal gasification have been made by several groups of workers in recent years (6, 7). These studies have dealt almost exclusively with the static state of catalyst. We wish to report here dynamic behaviors of catalyst on coal gasification observed by the SEM coupled with the energy dispersive analysis of X-rays (EDAX).

This technique would be useful in the following aspects. The movement of nickel particles can be monitored by examining the specimens before and after gasification. The relationship between the catalytic activity and the size or shape of nickel particle can be checked. A semi-quantitative analysis is possible with respects to the presence of mineral matter and its catalytic activity on the gasification. The interaction of nickel with other elements can be examined. The sulfur poisoning of nickel catalyst is the most important interaction among all. The present method, however, has some limitations in addition to the dangers implicit in the use of microscopy, which Thomas called as the twin evils of electricity and tendentiousness (3). The first limitation is that we did not observe the change of coal surface at reaction conditions, but at room temperature. Some changes might occur during the cooling stage. The second one is the neglect of possible catalytic activities of fine particles of diameter less than 100 nm. In spite of these limitations, we believe that this technique may give useful informations about the catalytic behavior of nickel particles.

EXPERIMENTAL

Coal samples used in this study were the same as in the earlier work (2). Ammonia treatment was carried out at 373 K and 10 MPa for 1 hr. About 1 wt% of nickel was impregnated on coal from an aqueous solution of hexaamminenickel(II) carbonate. Details on these pretreatments and analyses of coals were reported elsewhere (8). We would like to use the abbreviations for coal samples with different pretreatments; UN for raw coal, UC for raw coal with nickel catalyst, and TC for ammonia treated coal with nickel catalyst. The same nomenclatures are also used for the chars therefrom. For the SEM observations, five coal particles of 1 - 2 mm in size were mounted on a cylindrical graphite holder which is fit for the SEM equipment. Graphite paste was used to adhere the coal particles to the holder.

Figure 1 illustrates the reactor assembly. Two graphite sample holders were put on a rectangle quartz dish with a size of 20 by 40 mm. The dish can be moved horizontally by a quartz tube with a hook. In this quartz tube, a thermocouple was inserted to monitor the reaction temperature. The temperature difference between the tip of this thermocouple and the coal sample was less than 5 K. The furnace temperature was controlled by another thermocouple. For steam generation, a small evaporator with an electric heating wire was utilized. It evaporates water fed from a microfeeder at a constant rate. Exposed parts of tubings were also wound with a heating wire in order to prevent a steam condensation.

Coal samples on a graphite holder were examined under an SEM, a Hitachi-Akashi MSM 4C-101, to which an EDAX, a Horiba EMAX-1500, was attached. Then, the holder was put on a quartz dish and placed in the reactor. The initial position of the dish was outside of the furnace. After an evacuation of the system, nitrogen gas was introduced at the flow rate of 200 cm<sup>3</sup>(STP)/min. When the furnace temperature reached 773 K, the quartz dish was pushed into the center of the furnace. It was pulled out after the devolatilization for 1 hr. Samples were then carefully examined by SEM and EDAX. The graphite holder were returned to the quartz dish in the reactor. The evacuation of the system was followed by the introduction of nitrogen and reacting gas. In case of steam gasification, the flow rate of nitrogen was kept at 40 cm<sup>3</sup>(STP)/min and the flow rate of steam was 150 cm<sup>3</sup>(STP)/min. When the temperature and the gas flow rate became stationary, the quartz dish was pushed in. After the required time of gasification, the coal sample was pulled out to be examined. Similar procedures were repeated for several times to follow the morphological changes at the same sights on char surface. In case of hydrogasification, the flow rate of hydrogen was 200 cm<sup>3</sup>(STP)/min. Some photographs were taken for coal samples gasified in the thermobalance reported earlier (2).

The conversion of coal at each stage was determined in a different series of experiments. Coal particles of about 200 mg were placed on a quartz dish without graphite holders. The devolatilization and gasification were carried out under the same reaction conditions as before. At the end of each stage, the weight was measured and the conversion was calculated on a dry ash free basis.

## RESULTS AND DISCUSSIONS

We would like to mention first about the result of observation on coals without any heat treatment. Figure 2 shows the surface of Shin-Yubari coal cut by a microtome in order to check whether the nickel salt penetrated into the inside of particle. Three points should be noted here. First, the ammonia treated coal has cracks of various widths, whereas the untreated coal has no cracks. We present here only one particle for each, but this tendency was quite general one. The crack formation was particularly remarkable for lower rank coals. Second, the presence of nickel salt was recognized either on the external surface as in (b) or along the cracks as in (d). In these two photographs, the concentration of nickel was analyzed along the upper straight line, and it was shown as a notched line. These facts indicate that the nickel salt on a UC sample exists mainly on the external surface, whereas that on a TC sample exists not only on the external surface but also in the inside of coal particle. Third, there were many ellipsoidal holes of a diameter of about 10 μm on the cut surface. Flakes with a thickness of 1 μm were made during the course of cutting by a microtome, and it was also examined on SEM. We found that the flake consisted of many granular particles supported on a thin film. These particles might come out from the holes mentioned above. It can therefore be presumed that these holes are made because of the heterogeneity of coal in mechanical strength. Similar holes were observed for all other types of coal.

Table I. Successive Gasification of Leopold Coal

Stage	Gas	Temperature (K)	Reaction Time (hr)	Conversion (% daf)		
				UN	UC	TC
1	N <sub>2</sub>	773	1.0	26	25	23
2	H <sub>2</sub> O	1023	0.5	37	37	37
3	H <sub>2</sub> O	1023	0.5	40	41	42
4	H <sub>2</sub> O	1023	0.5	42	45	47
5	H <sub>2</sub> O	1073	0.5	49	55	56
6	H <sub>2</sub> O	1073	1.0	60	67	71

As an example of catalytic coal gasification, we present here the result on steam gasification of Leopold coal. The heat treatment procedures and the conversion on a dry ash free basis are summarized in Table I. The conversion was in accordance with that obtained earlier in a thermobalance (2). Figure 3 shows a typical behavior of nickel catalysts during steam gasification. At the first stage, where the coal was devolatilized in nitrogen, most nickel exist as flakes. Some granular nickel particles are seen in Figure 3(a). An X-ray diffraction analysis revealed that the state of nickel at this stage was already metallic. The dispersion of nickel is not homogeneous, and the accumulation of nickel along cracks is observed. A lesser amount of nickel is found on the flat surface at the upper left side of the photograph. At the second stage, most of flakes have changed to particles. The size of particle seems to be around a few microns so far as judging from Figure 3(b). However, in fact, each particle consists of a number of much smaller particles which are bundled in a wooly substance. In the upper left corner, many nickel particles appeared and they catalyzed the gasification around them, resulting in the formation of holes. Most of these particles disappeared in their own holes at the third stage (c). At the fifth stage (d), the surface becomes rough and rough. The nickel particles start to agglomerate. The ditch becomes wide. EDAX examined the nickel and sulfur concentration for the whole field of view in this series. It can be said that the nickel content decreased at the third stage perhaps due to the submersion of particles into holes. The sulfur content also decreased at this stage. The mechanism whereby this occurs is unclear. One possible explanation may be the desulfurization by an excess amount of steam and/or hydrogen. Figure 4 shows somewhat less common example. At the devolatilization stage, fine particles with diameters of less than 0.1  $\mu\text{m}$  gather to form a long, narrow strip. Fine cracks were observed on and near this strip. Some of them were perpendicular to the strip. After the gasification for 0.5 hr, a deep ditch appeared where fine particles had existed. Comparing with the depth of holes dug by an ordinal spherical particle shown on a flat surface, we may presume that the fine particle is much more active as a gasification catalyst. After the second stage, the gasification reaction proceeds in a similar manner as shown in Figure 3. In some cases, needle crystals containing nickel and a considerable amount of sulfur were observed after devolatilization. These were not so active.

Low magnification photographs of Leopold-UC coal and the first stage char are shown in Figure 5. A cubic particle swells upon devolatilization. The degree of swelling can be estimated by measuring the size of particle before and after the heat treatment. Usually, TC samples do not swell and some of UC samples swell as this particle does. Most of UN coal particles swell to some extent (FSI is  $1\frac{1}{2}$ ). Such suppression effect on caking property by the present pretreatment has been found for a variety of coals. Almost no nickel particles were observed on the hemispherical portion of char in Figure 5(b), which had bubbled out from the inside of coal. In order to check the uncatalyzed gasification rate, the change in this portion was followed throughout the series of steam gasification shown in

Table I. Practically no change was observed. Ash particles containing iron catalyzed the gasification, although the effect as catalyst was much smaller than that of nickel. Other ash particles containing aluminum, silicon, potassium, or calcium were found to be catalytically inactive.

Figure 6 shows two examples of the fate of nickel catalyst. Both samples are Leopold TC char gasified in steam at 1123 K for 2 hr. The conversion was 92 %. The first photograph indicates the accumulation of nickel and ash on the external surface of char particle at such a high conversion. Spot analyses by EDAX revealed the composition of ash as follows: A, nickel; B, nickel and sulfur; C, nickel; D and E; aluminum, silicon, nickel, iron and sulfur; F, iron; G, little sulfur, which means the main element is carbon. The blackish part which can be seen through the cleavage of ash layer is nearly pure carbon. The contact of this carbonaceous portion with nickel catalysts seems to be poor. The ash layer may be a resistance for gas diffusion. These facts imply the difficulty of catalyst utilization at high conversion. The second photograph shows the interior of Leopold char. This surface was exposed by cutting a char particle by a razor blade. The inside of char is very porous. In these macropores, few nickel particles were recognized. In accord with the observation in Figure 2, some nickel particles were found in the inside of TC char, but none in the inside of UC char. Anyhow, the amount was quite small compared with that present on the external surface. All other chars from different coals also have similar macropores. The amount of nickel in these macropores are also limited. In order to utilize nickel catalyst efficaciously, we should make all possible efforts to impregnate nickel salt not only on the external surface but also in the inside of coal particle.

Figure 7 exhibits some reactions of nickel with other elements in coal. A somewhat peculiar form of nickel is shown in the first photograph which was taken from Zollverein TC char. The intensity of EDAX tells us that a stick-shaped part is made from iron with a small amount of nickel, and that a ball-shaped part is made from nearly an equal amount of nickel and iron. The slender the stick, the larger the ratio of iron to nickel. The bigger the ball, the larger the nickel content. We think these are some compound resulted from the reaction of nickel and iron, although an X-ray diffraction study of char could not identify it. There is no evidence so far that they catalyze the gasification reaction. The reaction with sulfur is more important in connection with the catalyst poisoning (7). Sulfur exists all over the coal particle, and this reaction was observed quite frequently in case of steam gasification. As is shown in the line profiles of nickel and sulfur in Figure 7(b), some nickel particles contain a considerable amount of sulfur, while the others do not. The concentration of sulfur is not homogeneous even in a single particle. The catalytic activity of nickel does not seem to have a strong dependence on the sulfur content. We can find many nickel particles which is still active in spite of the contamination with sulfur. In the case of hydrogasification at 1273 K, the sulfur on nickel was quickly taken away as hydrogen sulfide. Essentially no sulfur remained after a few stages of hydrogasification.

#### CONCLUSIONS

A nickel catalyzed gasification of coal has been investigated by means of SEM and EDAX. We followed the movement of catalyst by observing the fixed sight before and after gasification. The most important finding is that nickel particles do not exist in the interior of coal particle so far as the present method of impregnation is utilized. Nickel particles on the external surface are found to be very active as catalysts. In other words, true reaction rate for catalytic gasification is much greater than non-catalytic reaction rate. If we can only find an appropriate method of impregnation to put nickel salt into the inside of

coal, the catalytic effect would be significantly improved. The next important result is the fact that the catalytic activity of nickel varies with the form of nickel particle. Very fine particle, for example, are much more active than the others. Thus, the second subject that we should challenge is to find an impregnation method which can disperse most nickel in the form of such very fine particles.

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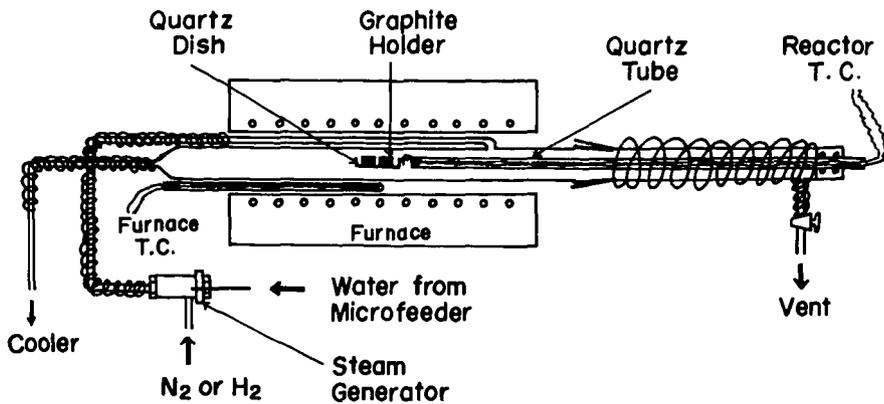


Fig. 1. Schematic diagram of apparatus

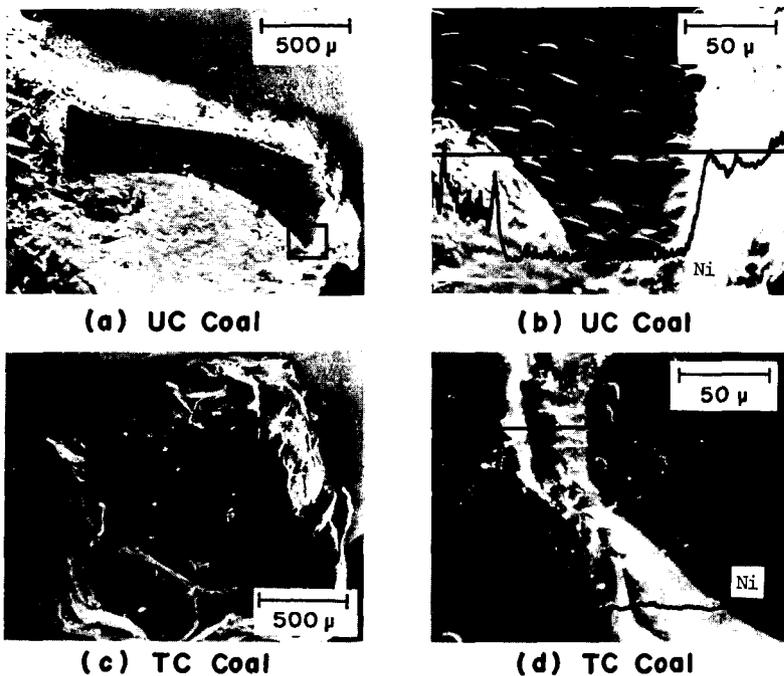
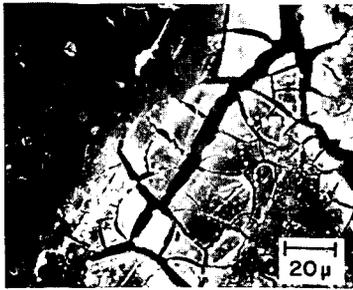
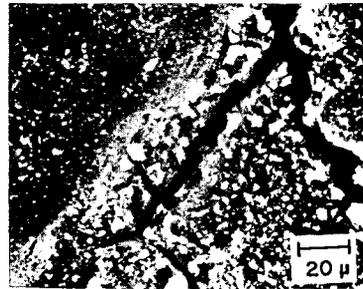


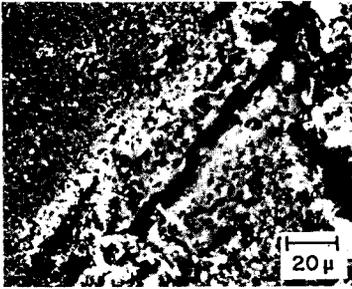
Fig. 2. Nickel Impregnated Shin-Yubari Coal



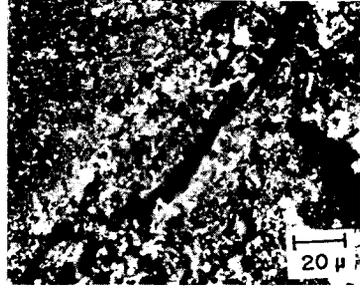
(a) 1st Stage



(b) 2nd Stage

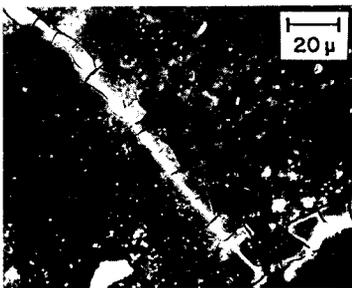


(c) 3rd Stage

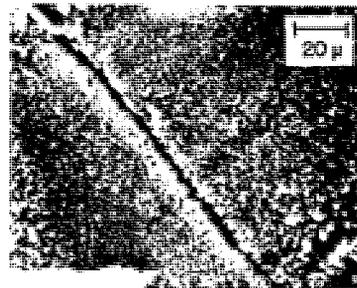


(d) 5th Stage

Fig. 3. Leopold TC Char (1)

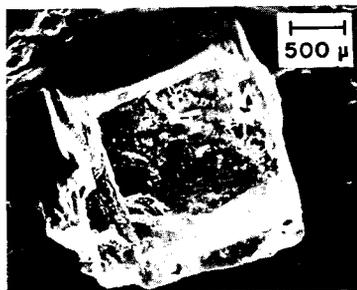


(a) 1st Stage

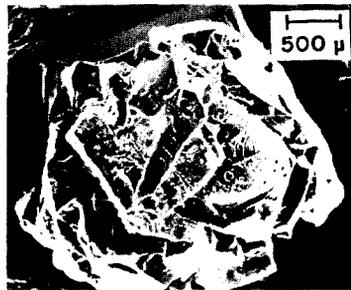


(b) 2nd Stage

Fig. 4. Leopold TC Char (2)

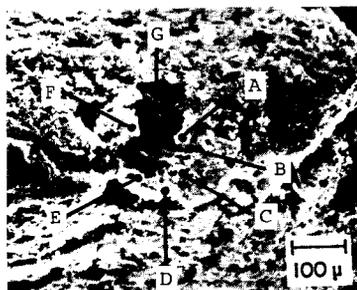


(a) Raw Coal

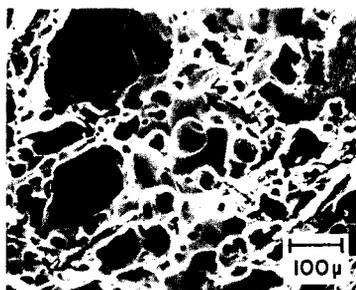


(b) 1st Stage Char

Fig. 5. Leopold UC Coal and Char



(a) Accumulation of Ash

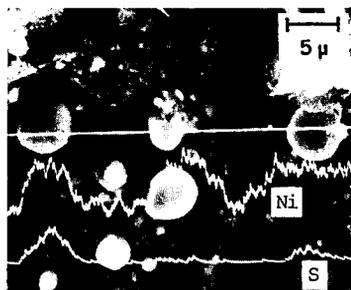


(b) Interior of Char

Fig. 6. Leopold Char at a Conversion of 92%



(a) Reaction with Fe



(b) Reaction with S

Fig. 7. Reaction of Nickel